


DECLARATION

I, Shusa ENDOH of SHIRAI INTERNATIONAL PATENT OFFICE,
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that I believe attached English version is a true complete translation of JP
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[NECESSITY OF PROOF] Necessary

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION] COATING COMPOSITION AND METHOD FOR
PRODUCING THE SAME

[CLAIMS]

5 [CLAIM 1] A coating composition comprising;

(a) at least one component selected from the group
consisting of an organosilane represented by the following
general formula (1) and a hydrolyzate of said organosilane;

(b) an organosiloxane oligomer having an SiO bond and a
10 weight average molecular weight of 300 to 100,000;

(c) a polymer containing a silyl group having a silicon
atom bound to a hydrolytic group and/or a hydroxyl group;

(d) a photocatalyst; and

(e-1) an organic solvent having a surface tension at 20°C
15 of 260 μ N/cm or less:



wherein, R^1 , which may be the same or different when two or more
 R^1 groups are present, represents a monovalent organic group
having 1 to 8 carbon atoms; R^2 , which may be the same or different
20 when two or more R^2 groups are present, represents an alkyl group
having 1 to 5 carbon atoms or an acyl group having 1 to 6 carbon
atoms; and n is an integer ranging from 0 to 2.

[CLAIM 2] The coating composition according to claim 1,
wherein said component (b) has a group represented by general
25 formula $-(RO)_p-(R'O)_q-R''$ (wherein R and R' , which may be the

same or different, represent alkyl groups each having 1 to 5 carbon atoms, R'' represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, and p+q is from 2 to 30), and a silyl group having a silicon atom bound to a hydrolytic group and/or a hydroxyl group.

[CLAIM 3] A method for producing a coating composition which comprises hydrolyzing and/or condensing at least one selected from the group consisting of;

(a) an organosilane represented by the following general formula (1);

(b) an organosiloxane oligomer having an SiO bond and a weight average molecular weight of 300 to 100,000; and

(c) a polymer containing a silyl group having a silicon atom bound to a hydrolytic group and/or a hydroxyl group, in the presence of

(d') an aqueous dispersion of a photocatalyst having a pH of 3 to 9 and

(e) an organic solvent in which the content of an organic solvent having a surface tension at 20°C of more than 260 $\mu\text{N}/\text{cm}$ is 20% by weight or less based on the whole organic solvent:



wherein, R^1 , which may be the same or different when two or more R^1 groups are present, represents a monovalent organic group having 1 to 8 carbon atoms; R^2 , which may be the same or different when two or more R^2 groups are present, represents

an alkyl group having 1 to 5 carbon atoms or an acyl group having 1 to 6 carbon atoms; and n is an integer ranging from 0 to 2.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

5 [RELEVANT TECHNICAL FIELD TO THE INVENTION]

The present invention relates to a coating composition excellent in dispersion stability of a photocatalyst, excellent in storage stability, giving a coating layer excellent in durability and adhesion, and having a photocatalytic function.

10 [0002]

[BACKGROUND OF THE INVENTION]

In recent years, compositions for coating have been desired which can form coating layers excellent in resistance to weather, resistance to stains and resistance to chemicals, and moreover high in hardness. Further, coating compositions having the increased versatility will be desired in future. So far, compositions comprised of silyl group-containing vinyl resins and organosilane compounds are described in Japanese Patent Laid-open Publication (Hei) 01-69673 and Japanese Patent Laid-open Publication (Hei) 01-69674. However, they are all limited in substrates. Such compounds are further described in Japanese Patent Laid-open Publication (Hei) 04-108172, Japanese Patent Laid-open Publication (Hei) 04-117473 and so forth. However, detailed coating specifications are not described therein, although subject substrates cover a wide

range.

[0003]

On the other hand, organosilane coating materials have technically been developed for use as maintenance-free coating materials excellent in resistance to weather (sunlight) and resistance to stains. The performance required for such organosilane coating materials increasingly become severe. In recent years, coating materials have been desired which can form coating layers excellent in coating appearance, adhesion, resistance to weather, heat, alkalis, organic chemicals, moisture and (hot) water, insulation durability, abrasion resistance and resistance to stains, and high in hardness.

[0004]

In particular, for improving resistance to stains, it is known that hydrophilization of surfaces of coating layers is suitable. For example, methods of adding hydrophilic materials or water-soluble materials to the coating composition are proposed. According to such methods, however, the hydrophilic materials or water-soluble materials are gradually deteriorated by light, or washed away with water, which makes it difficult to maintain the hydrophilicity of the surfaces of the coating layers at a sufficient level for a long period of time.

[0005]

In recent years, many compositions for coating in which

photocatalytic components are compounded have been proposed. For example, a method for forming an inorganic coating layer (Japanese Patent Laid-open Publication (Hei) 8-259891) is known in which 20 to 200 parts by weight of tetraalkoxysilane, 100 parts by weight of trialkoxysilane and 0 to 60 parts by weight of dialkoxysilane are used as raw materials, and a coating layer obtained from a mixed solution of an inorganic paint and a powder having a photocatalytic function is treated with an acid or an alkali, the inorganic paint being prepared from the raw materials and having a polystyrene-converted weight-average molecular weight of 900 or more, as well as a titanium oxide coating layer forming composition for a photocatalyst comprising titanium oxide, a hydrolyzate of a hydrolytic silicon compound (an alkyl silicate or a silicon halide) and a solvent (water or an alcohol) (Japanese Patent Laid-open Publication (Hei) 8-164334), and a surface treatment composition for imparting antibacterial and mildewproofing properties comprising a silicon compound having at least two alkoxyl groups, a titanium compound or zirconium compound having at least two alkoxyl groups and a hydrophilic inorganic powder such as alkoxysilane- and/or polysiloxane-treated titanium oxide having a guanidyl group (Japanese Patent Laid-open Publication (Hei) 8-176527).

[0006]

However, these compositions and mixed solution for

coating layer formation substantially aim at antibacterial and mildewproofing properties, deodorization and decomposition of injurious matter due to the photocatalytic components or alkoxy silane- and/or polysiloxane components having a guanidyl group. However, accompanying with above functions, coating layer performances required for organosilane coating materials, including hardness, adhesion, and resistance to alkalis, organic chemicals, weather and stains, are not studied overall.

[0007]

10 On the other hand, as coating compositions satisfying the required performance to some degree, there are proposed a composition in which a partial condensate of organosilane, a dispersion of colloidal silica and a silicone-modified acrylic resin are compounded (Japanese Patent Laid-open Publication 15 (Sho) 60-135465), a composition in which a condensate of organosilane, a chelate compound of zirconium alkoxide and a hydrolytic silyl group-containing vinyl resin are compounded (Japanese Patent Laid-open Publication (Sho) 64-1769), and a compound in which a condensate of organosilane, a colloidal 20 alumina and a hydrolytic silyl group-containing vinyl resin are compounded (U.S. Patent No. 4,904,721).

[0008]

However, coating layers obtained from the compositions disclosed in Japanese Patent Laid-open Publication (Sho) 25 60-135465 and U.S. Patent No. 4,904,721 described above have

the disadvantage that their luster is decreased by long-term irradiation of ultraviolet rays. Also, the composition disclosed in Japanese Patent Laid-open Publication (Sho) 64-1769 described above is insufficient in storage stability, and has the problem that an increase in solid concentration is liable to cause gelation within a short period of time.

[0009]

Further, the applicant of the present invention have already proposed a coating composition containing a hydrolyzate and/or a partial condensate of organosilane, a vinyl resin having a hydrolytic silyl group and/or a silyl group having a silicon atom bonded to a hydroxyl group, a metallic chelate compound, and a β -diketone and/or a β -keto ester (Japanese Patent Laid-open Publication (Hei) 5-345877). Although the composition is excellent in the balance of the above-mentioned coating layer performances required for any organosilane coating material, it is also required that these performances are further improved.

[0010]

Furthermore, in Japanese Patent Laid-open Publication (Hei) 9-227161, a self-cleaning film provided with a surface layer containing substantially transparent photocatalytic oxide particles is disclosed. However, the film is deteriorated in quality by a photocatalytic function for itself, thus a problem with regard to long-term durability is sometimes

raised. Furthermore, in Patent Laid-open Publication (Hei) 9-313887, a photocatalytic sheet provided with a photocatalytic layer on its surface and coated with an adhesive agent on the back thereof, thereby attaching it to another device or member to offer a photocatalytic function is proposed. However, the sheet is similarly deteriorated in quality by a photocatalytic function for itself, bringing a problem with regard to long-term durability.

[0011]

On the other hand, in the case that a photocatalyst (titanium dioxide) is used in the coating composition as an aqueous dispersion, the strong acidic aqueous dispersion is easily dispersible in an alcohol relatively high in hydrophobicity (for example, i-propyl alcohol or i-butyl alcohol), because of its excellent dispersion stability. However, the strong acidic aqueous dispersion brings problems such as corrosiveness to machines used in the production or coating of the resultant composition and the environmental safety. On the contrary, when aqueous titanium dioxide dispersion having a pH of 3 to 9 is used considering these problems, the problem of poor dispersion stability in the above-mentioned hydrophobic alcohol is encountered. When a solvent which can stabilize aqueous titanium dioxide dispersion having a pH of 3 to 9, for example, diethylene glycol monoethyl ether, is used for solving this problem, a cissing phenomenon

of the composition is sometimes observed on an undercoat layer such as intermediate layer or a substrate, because this solvent has high surface tension.

[0012]

5 [PROBLEM TO BE SOLVED BY THE INVENTION]

The present invention has been made against the background of the above-mentioned conventional technical problems, and it is an object of the invention to provide a coating composition excellent in dispersion stability of a photocatalyst even in a highly hydrophobic alcohol such as i-propyl alcohol, excellent in storage stability, giving a coating layer excellent in durability and adhesion, and having a photocatalytic function.

[0013]

15 [MEANS FOR SOLVING THE PROBLEMS]

According to the present invention, there is provided a coating composition comprising;

(a) at least one component selected from the group consisting of an organosilane represented by the following general formula (1) and a hydrolyzate of said organosilane (hereinafter referred to as "component (a)");

(b) an organosiloxane oligomer having an SiO bond and a weight average molecular weight of 300 to 100,000 (hereinafter also referred to as "component (b)");

25 (c) a polymer containing a silyl group having a silicon

atom bound to a hydrolytic group and/or a hydroxyl group (hereinafter also referred to as "component (c)" or "silyl group-containing polymer");

(d) a photocatalyst (hereinafter also referred to as "component (d)"); and

(e-1) an organic solvent having a surface tension at 20°C of 260 $\mu\text{N/cm}$ or less (hereinafter also referred to as "component (e-1)");



wherein, R^1 , which may be the same or different when two or more R^1 groups are present, represents a monovalent organic group having 1 to 8 carbon atoms; R^2 , which may be the same or different when two or more R^2 groups are present, represents an alkyl group having 1 to 5 carbon atoms or an acyl group having 1 to 6 carbon atoms; and n is an integer ranging from 0 to 2.

The above-mentioned component (b) may have a group represented by general formula $-(\text{RO})_p-(\text{R}'\text{O})_q-\text{R}''$ (wherein R and R' , which may be the same or different, represent alkyl groups each having 1 to 5 carbon atoms, R'' represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, and $p+q$ is from 2 to 30), and a silyl group having a silicon atom bound to a hydrolytic group and/or a hydroxyl group.

Further, the present invention provides a method for producing a coating composition which comprises hydrolyzing and/or condensing at least one selected from the group

consisting of component (a), component (b), and component (c),
in the presence of

(d') an aqueous dispersion of a photocatalyst having a
pH of 3 to 9 and

5 (e) an organic solvent in which the content of an organic
solvent having a surface tension at 20°C of more than 260 $\mu\text{N}/\text{cm}$
is 20% by weight or less based on the whole organic solvent
(hereinafter also referred to as "component (e)").

[0014]

10 [MODE FOR CARRYING OUT THE INVENTION]

Coating Composition

The coating composition of the present invention will be
described for each constituent feature.

Component (a):

15 Component (a) is at least one selected from an
organosilane represented by the above-mentioned general
formula (1) (hereinafter referred to as "organosilanes (1)")
and a hydrolyzate of the organosilane (1), and acts as a binder
in the composition of the invention. That is to say, component
20 (a) may be one or a mixture of all the two groups.

The above-mentioned hydrolyzate of organosilane (1) does
not require that two to four OR^2 groups generally contained in
organosilane (1) have all been hydrolyzed. For example, one
in which only one of the groups have been hydrolyzed or one in
25 which two or more of the groups have been hydrolyzed, or a mixture

thereof may be used.

When the hydrolyzate of organosilane (1) is used as component (a) as described above, organosilane (1) can be previously hydrolyzed to use the hydrolyzate as component (a).

5 However, when mixed with the remainder components to prepare the composition, organosilane (1) is preferably hydrolyzed by addition of a proper amount of water to form component (a).

In particular, it is preferred that organosilane (1) is hydrolyzed and condensed in the presence of the following
10 components (b) to (e), as described later.

In the present invention, components (a) can be used either alone or as a mixture of two or more of them.

[0015]

In general formula (1), the monovalent organic groups of
15 R^1 each having 1 to 8 carbon atoms include, for example, alkyl groups such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, n-hexyl, n-heptyl, n-octyl and 2-ethylhexyl; acyl groups such as acetyl, propionyl, butyryl, valeryl, benzoyl, toluoyl and caproyl; a vinyl group; an aryl
20 group; a cyclohexyl group; a phenyl group; an epoxy group; a glycidyl group; a (meth)acryloxy group; an ureido group; an amido group; a fluoroacetoamido group; an isocyanate group; and their substituent derivatives.

[0016]

25 The substituent groups in the substituent derivatives of

R¹ include, for example, halogen atoms, substituted or not-substituted amino groups, a hydroxyl group, a mercapto group, an isocyanate group, a glycidoxy group, a 3,4-epoxycyclohexyl group, a (meth)acryloxy group, an ureido group, and ammonium
5 bases. The number of carbon atoms in the substituent derivative of R¹ is 8 or less, including the carbon atoms in the substituent group.

When two R¹ groups are present in general formula (1), they may be the same or different.

10 [0017]

The alkyl groups of R² each having 1 to 5 carbon atoms include, for example, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, t-butyl and n-pentyl, and the acyl groups each having 1 to 6 carbon atoms include, for example, acetyl,
15 propionyl, butyryl, valeryl and caproyl.

A plurality of R² groups existing in general formula (1) may be the same or different.

[0018]

Specific examples of such organosilanes (1) include
20 methyltriacetyloxysilane and dimethyldiacetyloxysilane, as well as tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane, tetra-n-propoxysilane, tetra-i-propoxysilane and tetra-n-butoxysilane;
trialkoxysilanes such as methyltrimethoxysilane,
25 methyltriethoxysilane, ethyltrimethoxysilane, ethyltri-

ethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, i-propyltrimethoxysilane, i-propyltriethoxysilane, n-butyltrimethoxysilane, n-butyltriethoxysilane, n-pentyltrimethoxysilane, n-hexyltrimethoxysilane, 5 n-heptyltrimethoxysilane, n-octyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, cyclohexyltrimethoxysilane, cyclohexyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-chloropropyltriethoxysilane, 3,3,3-tri10 fluoropropyltrimethoxysilane, 3,3,3-trifluoropropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 2-hydroxyethyltrimethoxysilane, 2-hydroxyethyltriethoxysilane, 2-hydroxypropyltrimethoxysilane, 2-hydroxypropyltriethoxysilane, 3-hydroxypropyltrimethoxy15 silane, 3-hydroxypropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-isocyanatopropyltrimethoxysilane, 3-isocyanatopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltri20 methoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, 3-(meth)acryloxypropyltrimethoxysilane, 3-(meth)acryloxypropyltriethoxysilane, 3-ureidopropyltrimethoxysilane and 3-ureidopropyltriethoxysilane; and

[0019]

25 dialkoxysilanes such as dimethyldimethoxysilane, dimethyl-

diethoxysilane, diethyldimethoxysilane, diethyldiethoxysilane, di-n-propyldimethoxysilane, di-n-propyldiethoxysilane, di-i-propyldimethoxysilane, di-i-propyldiethoxysilane, di-n-butyldimethoxysilane, di-n-butyldiethoxysilane, 5 di-n-pentyldimethoxysilane, di-n-pentyldiethoxysilane, di-n-hexyldimethoxysilane, di-n-hexyldiethoxysilane, di-n-heptyldimethoxysilane, di-n-heptyldiethoxysilane, di-n-octyldimethoxysilane, di-n-octyldiethoxysilane, di-n-cyclohexyldimethoxysilane, di-n-cyclohexyldiethoxysilane, 10 diphenyldimethoxysilane, diphenyldiethoxysilane.

[0020]

Of these, the trialkoxysilanes and the dialkoxysilanes are preferred. The trialkoxysilanes are preferably methyltrimethoxysilane and methyltriethoxysilane, and the 15 dialkoxysilanes are preferably dimethyldimethoxysilane and dimethyldiethoxysilane.

[0021]

In the present invention, only the trialkoxysilane, or a combination of 40 to 95 % by weight of the trialkoxysilane 20 and 60 to 5 % by weight of the dialkoxysilane is preferred as organosilane (1). The use of the dialkoxysilane in combination with the trialkoxysilane causes a resultant coating layer to be softened and improved in resistance to alkalis.

[0022]

25 Component (b):

Component (b) is a siloxane oligomer having an SiO bond and a weight average molecular weight of 300 to 100,000.

Component (b) can be used either alone or as a mixture of two or more of them. Although there is no particular limitation

5 on a method for producing component (b), chlorosilane condensates and alkoxysilane condensates are mainly preferred.

In the above-mentioned siloxane oligomers, the functional groups introduced into the ends or the side chains of the siloxanes include groups represented by $-(RO)_p-(R'O)_q-R''$

10 (wherein R and R', which may be the same or different, represent alkyl groups each having 1 to 5 carbon atoms, R'' represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, and $p+q$ is from 2 to 30), as well as a hydroxyl group, halogen atoms

and organic groups each having 1 to 15 carbon atoms (such as 15 alkyl, acyl, alkoxyl, alkoxysilyl, vinyl, allyl, acetoxyl, acetoxysilyl, cycloalkyl, phenyl, glycidyl, (meth)acryloxy, ureido, amido, fluoroacetamide and isocyanate). These groups may be partially hydrolyzed or condensed, and may be substituted derivatives thereof.

20 [0023]

The above-mentioned halogen atoms include fluorine and chlorine.

The alkyl groups each having 1 to 15 carbon atoms include methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, 25 t-butyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, undecyl,

dodecyl, tridecyl, tetradecyl, hexadecyl, heptadecyl, octadecyl and 2-ethylhexyl. The acyl groups include acetyl, propionyl, butyl, valeryl, benzoyl and toluoyl. The alkoxyl groups include methoxy, ethoxy, propoxy and butoxy, and
5 alkoxysilyl groups include methoxysilyl, ethoxysilyl, propoxysilyl and butoxysilyl.

The groups represented by $-(RO)_p-(R'O)_q-R''$ are polyoxyalkylene groups such as polyoxyethylene, polyoxypropylene and poly(oxyethylene/oxypropylene). Component (b)
10 has such an end functional group, which causes a co-condensate of component (a) and component (b) to have hydrophilicity. In addition, a polyoxyalkylene portion is liable to be adsorbed by component (d), so that the dispersion stability of component (d) is improved.

15 [0024]

Examples of the substituent groups in the above-mentioned substituted derivatives include halogen atoms, substituted or unsubstituted amino groups, a hydroxyl group, a mercapto group, an isocyanato group, a glycidoxy group, a 3,4-epoxycyclohexyl
20 group, a (meth)acryloxy group, a ureido group, ammonium salt groups and keto ester groups.

[0025]

The weight average molecular weight (hereinafter also referred to as "Mw") of component (b) is preferably from 300
25 to 100,000, and particularly preferably from 600 to 50,000.

Less than 300 sometimes results in poor flexibility of the resultant coating layer, whereas exceeding 100,000 unfavorably lead to poor storage stability of the resultant coating composition in some cases.

5 A mixture of two kinds of oligomers different in Mw may be used as component (b). for example, a mixture of an oligomer having an Mw of 400 to 2,800 and an oligomer having an Mw of 3,000 to 50,000 may be used.

[0026]

10 Components (b) are commercially available as silicone resin manufactured by Dow Corning Toray Silicone Co., Ltd., silicone resin manufactured by Toshiba Silicone Co., silicone resin manufactured by Shin-Etsu Chemical Co., Ltd., hydroxyl group-containing polydimethylsiloxane manufactured by Dow
15 Corning Asia Co., Ltd., and a silicon oligomer manufactured by Nippon Unicar Company Limited. They may be used as such or as condensates.

In the present invention, components (b) may be used either alone or as a mixture of two or more of them.

20 [0027]

As to the amounts of component (a) and component (b) used, the amount of component (a) is from 5 to 95 % by weight, and preferably from 10 to 90% by weight, and the amount of component (b) is from 5 to 95 % by weight, and preferably from 10 to 90%
25 by weight (with the proviso that (a)+(b) = 100% by weight). When

the amount of component (a) is less than 5% by weight, the resultant coating composition sometimes becomes poor in curing properties. On the other hand, exceeding 95% by weight results in decreased crack resistance in some cases.

5 [0028]

In the composition of the present invention, component (b) is usually co-hydrolyzed and co-condensed together with component (a) described above.

10 In this case, the amount of water used for hydrolysis/condensation of organosilane (1) and component (b) is usually 0.3 mole or more, and preferably from about 0.4 to about 2 moles, based on mole of the total amount of organosilane (1) and component (b). When an aqueous dispersion of a photocatalyst is used as component (d), water existing in the
15 aqueous dispersion can be used for hydrolysis of organosilane (1) and component (b).

In the hydrolysis/reduction reaction in this case, that is to say, in the reaction in the preparation of the composition of the present invention, the reaction temperature is from 30°C
20 to 80°C, preferably from 40°C to 70°C, and the reaction time is from about 0.5 hour to about 10 hours, and preferably from about 1 hour to about 7 hours.

In the composition of the present invention, when component (a) and component (b) are co-hydrolyzed and co-
25 condensed, the weight average molecular weight of the co-

hydrolyzate /co-condensate (co-hydrolyzate and/or co-condensate) is usually from about 500 to about 100,000, and preferably from about 600 to about 80,000.

[0029]

5 Silyl Group-Containing Polymer (c):

Component (c) is a polymer in which a silyl group having a silicon atom bonded to a hydrolytic group and/or a hydroxyl group (hereinafter referred to as a "specific silyl group"), preferably at an end and/or a side chain of a molecular chain
10 of the polymer.

In the composition of the present invention, silyl group-containing polymer (c) is a component that brings about excellent coating layer performances by co-condensation of the hydrolytic group and/or the hydroxyl group of the silyl group
15 with component (a) described above in curing the coating layer.

The content of silicon atoms in component (c) is generally from 0.001 to 20% by weight, and preferably from 0.01 to 15% by weight, based on the whole component (c).

The preferred specific silyl group is a group expressed
20 by the following general formula (2):

[0030]



25 wherein, X represents a hydrolytic group such as a halogen atom, an alkoxyl group, an acetoxy group, a phenoxy group, a

thioalkoxyl group or an amino group, or a hydroxyl group, R^3 represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an aralkyl group having 1 to 10 carbon atoms, and i is an integer ranging from 1 to 3.

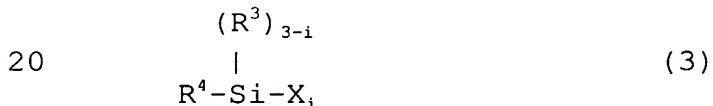
5 [0031]

Component (c) can be produced, for example, by methods described in the following (A) and (B):

(A) A method of allowing a hydrosilane compound corresponding to the above-mentioned general formula (2)
10 (hereinafter referred to as "hydrosilane compound (A)") to react with a carbon-carbon double bond in a carbon-carbon double bond-containing vinyl polymer (hereinafter referred to as an "unsaturated vinyl polymer") by addition reaction; and

[0032]

15 (B) A method of copolymerizing a silane compound represented by the following general formula (3) (hereinafter referred to as "unsaturated silane compound (B)") with another vinyl monomer:



wherein, X , R^3 and i each have the same meanings as given for X , R^3 and i in general formula (2), and R^4 represents an organic group having a polymerizable double bond.

25 [0033]

Hydrosilane compounds (A) used in the method of (A)

described above include, for example, halogenated silanes such as methyldichlorosilane, trichlorosilane and phenyldichlorosilane, alkoxysilanes such as methyldimethoxysilane, methyldiethoxysilane, phenyldimethoxysilane, trimethoxysilane and triethoxysilane, acyloxysilanes such as methyl-
5 diacetoxysilane, phenyldiacetoxysilane and triacetoxysilane, and aminoxysilanes such as methyldiaminoxysilane, triaminoxysilane and dimethylaminoxysilane.

These hydrosilane compounds (A) can be used either alone
10 or as a mixture of two or more of them.

[0034]

There is no particular limitation on the unsaturated vinyl polymers used in the method of (A) described above, as long as they are polymers other than hydroxyl group-containing
15 polymers. The unsaturated vinyl polymers can be produced by a method of (A-1) or (A-2) described below or a combination thereof.

(A-1) A method of (co)polymerizing a vinyl monomer having a functional group (hereinafter referred to as "functional
20 group (α)"), and then, reacting an unsaturated compound having a functional group which can react with functional group (α) (hereinafter referred to as "functional group (β)") and a carbon-carbon double bond with functional group (α) in the co(polymer), thereby producing the unsaturated vinyl polymer
25 having carbon-carbon double bonds at side chains of a molecular

chain of the polymer.

[0035]

(A-2) A method of (co)polymerizing a vinyl monomer, using a radical polymerization initiator having functional group (α) (for example, 4,4-azobis-4-cyanovaleric acid or the like), or using a radical polymerization initiator and a chain transfer agent both having functional group (α) (for example, 4,4-azobis-4-cyanovaleric acid and dithioglycolic acid), to synthesize a (co)polymer having functional group (α) derived from the radical polymerization initiator or the chain transfer agent at one end or both ends of a molecular chain of the polymer, and then, reacting an unsaturated compound having functional group (β) and a carbon-carbon double bond with functional group (α) in the (co)polymer, thereby producing the unsaturated vinyl polymer having the carbon-carbon double bond(s) at one end or both ends of the molecular chain of the polymer.

[0036]

Examples of the reactions of functional group (α) with functional group (β) in the methods of (A-1) and (A-2) include the esterification reaction of a carboxyl group with a hydroxyl group, the ring-opening esterification reaction of a carboxylic anhydride group with a hydroxyl group, the ring-opening esterification reaction of a carboxyl group with an epoxy group, the amidation reaction of a carboxyl group with an amino group, the ring-opening amidation reaction of a carboxylic anhydride

group with an amino group, the ring-opening addition reaction of an epoxy group with an amino group, the urethanation reaction of a hydroxyl group with an isocyanate group, and a combination of these reactions.

5 [0037]

The vinyl monomers having functional group (α) include, for example, unsaturated carboxylic acids such as (meth)acrylic acid, crotonic acid, maleic acid, fumaric acid, itaconic acid and so forth; unsaturated carboxylic anhydrides such as maleic anhydride and itaconic anhydride; hydroxyl group-containing vinyl monomers such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, N-methylol (meth)acrylamide and 2-hydroxyethyl vinyl ether; amino group-containing vinyl monomers such as 2-aminoethyl (meth)acrylate, 2-aminopropyl (meth)acrylate 3-aminopropyl (meth)acrylate and 2-aminoethyl vinyl ether; amineimido group-containing vinyl monomers such as 1,1,1-trimethylamine(meth)acrylimide, 1-methyl-1-ethylamine(meth)acrylimide, 1,1-dimethyl-1-(2-hydroxypropyl)amine(meth)acrylimide, 1,1-dimethyl-1-(2'-phenyl-2'-hydroxyethyl)amine(meth)acrylimide and 1,1-dimethyl-1-(2'-hydroxy-2'-phenoxypropyl)amine(meth)acrylimide; and epoxy group-containing vinyl monomers such as glycidyl (meth)acrylate and allyl-glycidyl (meth)acrylate.

25 These functional group (α)-containing vinyl monomers can

be used either alone or as a mixture of two or more of them.

[0038]

The other vinyl monomers copolymerizable with the functional group (α)-containing vinyl monomers include, for
5 example,

(A) aromatic vinyl monomers such as styrene, α -methylstyrene, 4-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methoxystyrene, 2-hydroxymethylstyrene, 4-ethylstyrene, 4-ethoxystyrene, 3,4-dimethylstyrene, 3,4-diethylstyrene,
10 styrene, 2-chlorostyrene, 3-chlorostyrene, 4-chloro-3-methylstyrene, 4-t-butylstyrene, 2,4-dichlorostyrene, 2,6-dichlorostyrene and 1-vinylnaphthalene;

[0039]

(B) (meth)acrylate compounds such as methyl (meth)-
15 acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, amyl (meth)-acrylate, i-amyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate and cyclohexyl (meth)acrylate;

20 [0040]

(C) multi-functional monomers such as divinylbenzene, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, propylene glycol
25 di(meth)acrylate, dipropylene glycol di(meth)acrylate, tri-

propylene glycol di(meth)acrylate, tetrapropylene glycol di(meth)acrylate, butanediol di(meth)acrylate, hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate and pentaerythritol tetra(meth)acrylate;

5 [0041]

(D) acid amide compounds such as (meth)acrylamide, N-methylol(meth)acrylamide, N-methoxymethyl(meth)acrylamide, N-butoxymethyl(meth)acrylamide, N,N'-methylenebisacrylamide, diacetoneacrylamide, maleamide and maleimide;

10 (E) vinyl compounds such as vinyl chloride, vinylidene chloride and fatty acid vinyl esters;

(F) aliphatic conjugated dienes such as 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-neopentyl-1,3-butadiene, 2-chloro-1,3-butadiene, 2-cyano-
15 1,3-butadiene, isoprene, straight-chain substituted conjugated pentadiene substituted by a substituent group such as an alkyl group, a halogen atom, a cyano group or the like and straight-chain or side-chain conjugated hexadiene;

[0042]

20 (G) vinyl cyanide compounds such as acrylonitrile and methacrylonitrile;

(H) fluorine atom-containing monomers such as trifluoroethyl (meth)acrylate and pentadecafluorooctyl (meth)acrylate;

25 (I) piperidine monomers such as 4-(meth)acryloyloxy-

2,2,6,6,-tetramethylpiperidine, 4-(meth)acryloylamino-
2,2,6,6-tetramethylpiperidine and 4-(meth)acryloyloxy-
1,2,2,6,6-pentamethylpiperidine;

(J) ultraviolet absorptive group-containing monomers
5 such as 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzo-
triazole, 2-(2'-hydroxy-3'-t-butyl-5'-methacryloxyethyl-
phenyl)-2H-benzotriazole, 2-hydroxy-4-(methacryloxy-
ethoxy)benzophenone and 2-hydroxy-4-(acryloyloxyethoxy)-
benzophenone; and besides, dicalpolactone.

10 These can be used either alone or as a combination of two
or more of them.

[0043]

The unsaturated compounds having functional group (β) and
carbon-carbon double bonds include, for example, vinyl monomers
15 similar to the functional group (α)-containing vinyl monomers,
isocyanate group-containing unsaturated compounds obtained by
the equimolar reaction of the above-mentioned hydroxyl
group-containing vinyl monomers with diisocyanate compounds.

[0044]

20 Specific examples of unsaturated silane compound (B) used
in the method of (B) described above include

$\text{CH}_2=\text{CHSi}(\text{CH}_3)(\text{OCH}_3)_2$, $\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$, $\text{CH}_2=\text{CHSi}(\text{CH}_3)\text{Cl}_2$,
 $\text{CH}_2=\text{CHSiCl}_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_2\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$,
 $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$,
25 $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$,

$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_2\text{SiCl}_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)\text{Cl}_2$,

$\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{SiCl}_3$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$,

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$,

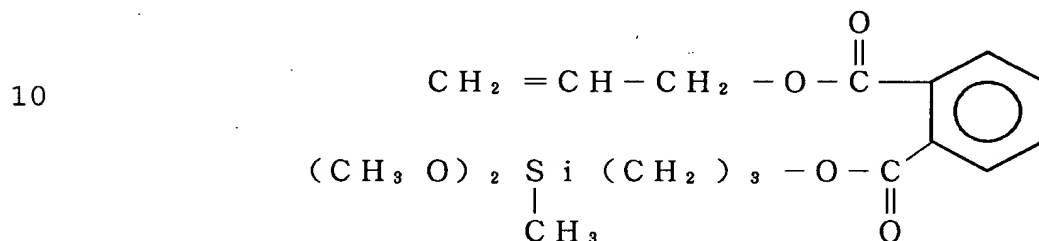
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$,

5 $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{SiCl}_3$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{CH}_3)\text{Cl}_2$,

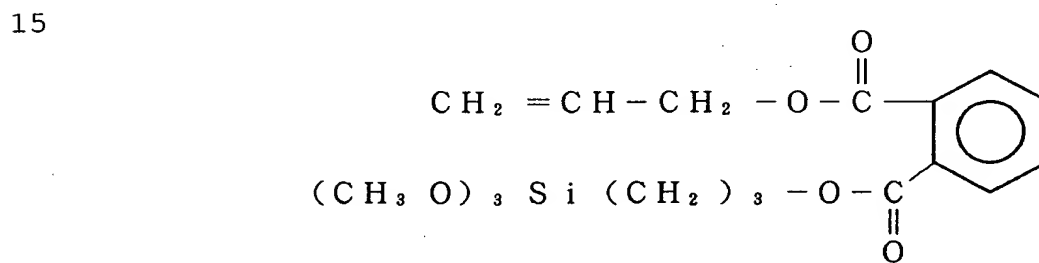
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{SiCl}_3$,

[0045]

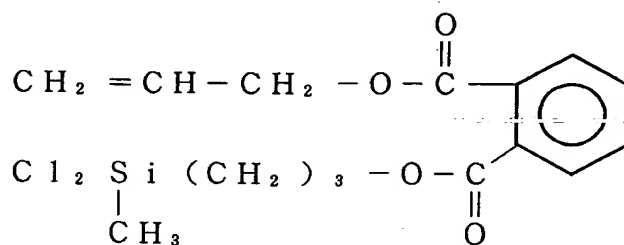
[CHEMICAL FORMULA 1]



[CHEMICAL FORMULA 2]

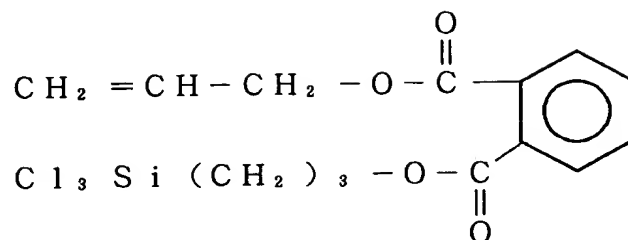


20 [CHEMICAL FORMULA 3]



and

[CHEMICAL FORMULA 4]



[0046]

These can be used either alone or as a combination of two
10 or more of them.

Further, the other vinyl monomers copolymerized with
unsaturated silane compound (B) include, for example, one or
more of the functional group (α)-containing vinyl monomers
exemplified in the method of (A-1) described above and other
15 vinyl monomers.

[0047]

Further, other examples of component (c) include specific
silyl group-containing epoxy resins and specific silyl
group-containing polyester resins.

20 The above-mentioned specific silyl group-containing
epoxy resins can be produced, for example, by allowing epoxy
groups in epoxy resins such as bisphenol A type epoxy resins,
bisphenol F type epoxy resins, hydrogenated bisphenol A type
epoxy resins, aliphatic polyglycidyl ethers and aliphatic
25 polyglycidyl esters to react with aminosilanes, vinylsilanes,

carboxysilanes and glycidylsilanes having the specific silyl groups.

Further, the above-mentioned specific silyl group-containing polyester resins can be produced, for example, by
5 allowing carboxyl groups or hydroxyl groups contained in polyester resins to react with aminosilanes, carboxysilanes, or glycidylsilanes having the specific silyl groups.

[0048]

The Mw of component (c) is preferably from 2,000 to 100,000,
10 and more preferably from 4,000 to 50,000.

The amount of component (c) used in the composition of the present invention is generally from 2 to 900 parts by weight, preferably from 10 to 400 parts by weight, and more preferably from 20 to 200 parts by weight, based on 100 parts by weight
15 of the total amount of the complete hydrolyzate/condensate of component (a) and component (b). In this case, when the amount of component (c) used is smaller than 2 parts by weight, the resultant coating layer is sometimes deteriorated in resistance to alkalis. On the other hand, exceeding 900 parts by weight
20 results in the tendency of long-term weather resistance of the coating layer to be lowered.

The term "complete hydrolyzate/condensate" described above means a product in which 100% of R^2O- groups of component (a) and component (b) are hydrolyzed to SiOH groups, which are
25 further completely condensed to give a siloxane structure.

[0049]

Polymerization processes used in producing the above-mentioned component (c) include, for example, a process of adding a monomer or monomers all at once for polymerization, a process of polymerizing some of a monomer or monomers and then continuously or intermittently adding the remaining monomer or monomers, and a process of adding a monomer or monomers in succession from the beginning of polymerization. Also, any combination of the polymerizing processes may be employed. Preferred examples of the polymerization processes include solution polymerization. As solvents used in the solution polymerization, ordinary ones can be used. Of these, ketones and alcohols are preferred. In the polymerization, known polymerizing initiators, molecular weight modifiers, chelating agents and inorganic electrolytes can be used.

[0050]

In the present invention, the above-mentioned component (c) can be used either alone or as a mixture of two or more obtained as described above.

[0051]

Photocatalyst (d):

Preferred examples of photocatalysts (d) include powders and/or sols of semiconductors having photocatalytic ability.

[0052]

The semiconductors having photocatalytic ability include,

for example, TiO_2 , TiO_3 , SrTiO_3 , FeTiO_3 , WO_3 , SnO_2 , Bi_2O_3 , In_2O_3 ,
 ZnO , Fe_2O_3 , RuO_2 , CdO , CdS , CdSe , GaP , GaAs , CdFeO_3 , MoS_2 , LaRhO_3 ,
 GaN , CdP , ZnS , ZnSe , ZnTe , Nb_2O_5 , ZrO_2 , InP , GaAsP , InGaAlP ,
 AlGaAs , PbS , InAs , PbSe and InSb . Of these, preferred are TiO_2
5 and ZnO , and particularly preferred is TiO_2 containing an
anatase type structure.

[0053]

In the present invention, it has become clear that the
photocatalytic ability of component (d) hydrophilizes a surface
10 of the coating layer for a short period of time even by poor
light, resulting in significant improvement in the resistance
to stains of the coating layer without substantial impairment
of other coating layer performances. Moreover, component (d)
is usually bonded to the above-mentioned component (a) and so
15 forth in the coating layer obtained from the composition of the
present invention, so that the hydrophilicity and resistance
to stains of the coating layer are maintained for a long period
of time.

[0054]

20 Further, it is desirable to use the above-mentioned
semiconductors in powder and/or sol form. In detail, any one
of the three kinds of a powder, an aqueous sol dispersed in water,
and a solvent sol dispersed in a polar solvent such as isopropyl
alcohol or a nonpolar solvent such as toluene is desirably used.
25 In the case of the solvent sol, the solvent sol may be further

diluted with water or a solvent, depending on the dispersion stability of the semiconductors. It is preferred that the average particle size of the semiconductors in these existing forms is as small as possible from the viewpoint of photocatalytic ability. In this case, when the average particle size of the semiconductors is 0.3 μm or more, the coating layers are liable to become opaque by the light covering function of the semiconductors. Less than 0.3 μm tends to cause the coating layers to be transparent. Accordingly, the average particle size of the semiconductors can be properly selected depending on the purpose of the compositions.

[0055]

When component (d) is the aqueous sol or the solvent sol, the solid concentration is preferably 50% by weight or less, and more preferably 40% by weight or less.

[0056]

As component (d) used in the present invention, it is desirable to use aqueous dispersion (d') preferably having a pH of 3 to 9, as described in the method for producing the composition of the present invention given later. The use of aqueous dispersion (d') having a pH of 3 to 9 preferably results in reduced corrosiveness to a machine used in the production or coating of the resultant composition and decreased environmental problems.

[0057]

As a method for adding component (d) to the composition, component (d) may be added after the preparation of a composition comprising the above-mentioned components (a) to (c), and components (e) to (j) described later, or can also be added in preparing this composition to hydrolyze and condense components (a) to (c) in the presence of component (d). When component (d) is added in preparing the composition, the semiconductor compound in component (d) can be co-condensed with component (a) to particularly improve the long-term durability of the resultant coating layer. When component (d) is the aqueous dispersion, it is preferably added in preparing the composition. Also when the viscosity in a system is increased by compounding of component (h) described later, the addition of component (d) in preparing the composition is preferred. Further, when the composition of the invention is used as an enamel containing a coloring component, toning may be carried out after the addition of component (d) to the composition, or component (d) and the coloring component may be added to the composition at the same time.

In particular, as described later, it is preferred that components (a) to (c) are hydrolyzed and condensed in the presence of (d') a photocatalyst dispersion having a pH of 3 to 9 and (e) an organic solvent in which the content of an organic solvent having a surface tension at 20°C of more than 260 $\mu\text{N/cm}$ is 20% by weight or less based on the whole organic solvent.

This causes photocatalyst (d) to be co-condensed with component (a). Thus, the resultant composition can be easily dispersed in an alcohol relatively high in hydrophobicity (such as i-propyl alcohol or i-butyl alcohol), and the wettability of the resultant composition to a substrate is improved, resulting in excellent film-forming properties of the resultant coating layer. Further, the composition excellent in storage stability is obtained.

[0058]

10 In the invention, components (d) can be used either alone or as a mixture of two or more of them.

The amount of component (d) used is usually from 1 to 500 parts by weight, and preferably from 5 to 400 parts by weight, in terms of the solid content, based on 100 parts by weight of the complete hydrolyzate/condensate of components (a) and (b). Less than 1 part by weight results in the lack of the stain proof effect due to the photocatalytic reaction in some cases, whereas exceeding 500 parts by weight sometimes results in a reduction in film-forming properties of the resultant coating composition.

[0059]

Organic Solvent (e):

Component (e-1):

Component (e-1) is an organic solvent having a surface tension at 20°C of 260 $\mu\text{N}/\text{cm}$ or less. Such organic solvent (e-1)

is low in surface tension, so that the resultant composition has good wettability to a substrate. Accordingly, a so-called "cissing phenomenon" is difficult to occur, and the resultant coating layer is excellent in film-forming properties.

5 The organic solvents (e-1) having a surface tension at 20°C of 260 μ N/cm or less include methyl alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, i-butyl alcohol, methyl ethyl ketone, methyl isobutyl ketone and butyl acetate.

 These organic solvents (e-1) may be used either alone or
10 as a combination of two or more of them.

[0060]

Component (e-2):

 In the composition of the present invention, an organic solvent having a surface tension at 20°C of more than 260 μ N/cm
15 can also be used in an amount of 20% by weight or less based on the whole organic solvent, in addition to the above-mentioned component (e-1). When component (e-2) is used in an amount of more than 20% by weight based on the whole organic solvent, the surface tension of the whole organic solvent is sometimes
20 increased too high, which may cause the resultant composition to bring about cissing to a substrate.

 Organic solvents having a surface tension at 20°C of more than 260 μ N/cm (e-2) include ethylene glycol monoethyl ether,
ethylene glycol monobutyl ether, diethylene glycol monoethyl
25 ether and cyclohexanone.

That is to say, when two or more kinds of organic solvents are used in combination in organic solvent (e) of the present invention, the average surface tension of the organic solvents is only required to be 270 $\mu\text{N}/\text{cm}$ or less. In other words, with
5 respect to the present composition, it is preferred that an organic solvent in which the content of an organic solvent having a surface tension at 20°C of more than 260 $\mu\text{N}/\text{cm}$ is 20% by weight or less based on all organic solvents added in the above-mentioned hydrolysis/condensation, in the storage of the
10 composition and in coating.

[0061]

The above-mentioned organic solvents (e) may be used either alone or as a combination of two or more of them.

Further, the amount of organic solvent (e) used can be
15 appropriately increased or decreased depending on the solid concentration of the composition of the present invention, as described later.

[0062]

In the composition of the present invention, components
20 (f) to (j) described later can be further used as required.

[0063]

Component (f):

Colloidal silica and/or colloidal alumina may be added to the composition of the present invention as component (f).

25 Component (f) can be added to the coating composition of

the present invention, thereby reducing the content of a photocatalyst such as titanium oxide without a substantial decrease of photocatalytic activity (hydrophilization ability). Further, a reduction in the content of a photocatalyst having organic material degradation ability can improve the durability of the substrate/coating layer.

Colloidal silica or colloidal alumina is, for example, a dispersion in water or an organic solvent. Usually, the average particle size is 1 μm or less, and preferably 0.5 μm or less, and the solid concentration is from about 10% to about 40% by weight.

Such colloidal silica includes, for example, Methanol Silica Sol and Isopropanol Silica Sol manufactured by Nissan Chemical Industries Ltd.; and Oscal manufactured by Catalyst & Chemicals Industries Co., Ltd. Colloidal alumina includes, for example, Alumina Sol-520, Alumina Sol-100 and Alumina Sol-200 manufactured by Nissan Chemical Industries Ltd.; and Alumina Clear Sol, Alumina Sol 10 and Alumina Sol 132 manufactured by Kawaken Fine Chemical Co., Ltd. Colloidal silica and/or colloidal alumina (f) described above can be used either alone or as a combination of two or more of them.

As component (f) contained in the composition of the present invention, colloidal silica is particularly preferred.

[0064]

The amount of component (f) used in the composition of

the present invention is generally from 5 to 500 parts by weight, preferably from 10 to 400 parts by weight, and more preferably from 20 to 200 parts by weight, in terms of the solid content, based on 100 parts by weight of the total amount of the complete hydrolyzate/condensate of component (a) and component (b). When the amount of component (f) is less than 5 parts by weight, sufficient hydrophilicity can not be obtained resulting in lower hydrophilic speed of the coating layer causing delayed revelation of resistance to stains in some cases. Whereas exceeding 500 parts by weight, the resultant coating composition is deteriorated in film-forming properties, resulting in development of cracks and separation in some cases.

[0065]

Component (g):

Component (g) is a catalyst for enhancing the hydrolysis and condensation reaction of components (a) to (c).

The use of component (g) will accelerate the curing speed of the resultant coating layer and increase the molecular weight of polysiloxane produced by the polycondensation reaction of the organosilane component, hence allowing the resultant coating layer to be improved in strength, long-term and durability, and increasing the thickness of the coating layer and facilitating the coating operation.

[0066]

Such component (g) is preferably an acidic compound, a

basic compound, a salt compound, an amine compound, an organometallic compound and/or a partial hydrolyzate thereof (the organometallic compound and/or the partial hydrolyzate thereof is hereinafter collectively referred to as "an organometallic compound, etc.>").

The above-mentioned acidic compounds include, for example, acetic acid, hydrochloric acid, sulfuric acid, phosphoric acid, alkyltitanic acids, p-toluenesulphonic acid and phthalic acid, and preferred is acetic acid.

Further, the above-mentioned basic compounds include, for example, sodium hydroxide and potassium hydroxide, and preferred is sodium hydroxide.

Furthermore, the above-mentioned salt compounds include, for example, alkali metal salts of naphthenic acid, octylic acid, nitrous acid, sulfurous acid, aluminic acid and carbonic acid.

[0067]

The above-mentioned amine compounds include, for example, various modified amines used as hardeners for epoxy resins, as well as ethylenediamine, hexamethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, piperidine, piperadine, m-phenylenediamine, p-phenylenediamine, ethanolamine, triethylamine, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-(2-aminoethyl)aminopropyltrimethoxysilane, 3-(2-aminoethyl)aminopropyltriethoxysilane, 3-(2-aminoethyl)aminopropylmethyldi-

methoxysilane, 3-anilinopropyltrimethoxysilane, alkylamine salts and quaternary ammonium salts, and preferred are 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane and 3-(2-aminoethyl)aminopropyltrimethoxysilane.

5 [0068]

Further, the above-mentioned organometallic compounds, etc. include, for example, compounds expressed by the following general formula (4) (hereinafter referred to as "organometallic compounds (4)"), organometallic compounds of tetravalent tin
10 each having 1 or 2 alkyl groups each having 1 to 10 carbon atoms, the alkyl groups being bonded to the same tin atom (hereinafter referred to as "organic tin compounds"), and partial hydrolyzates of these compounds.

[0069]

15 $M(OR^5)_r(R^6COCHCOR^7)_s$ (4)

wherein M represents zirconium, titanium or aluminum, R^5 and R^6 , which may be the same or different, each represent monovalent hydrocarbon groups each having 1 to 6 carbon atoms such as ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, t-butyl, n-pentyl,
20 n-hexyl, cyclohexyl or phenyl, R^7 represents an alkoxyl group having 1 to 16 carbon atoms such as methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, t-butoxy, lauryloxy or stearyloxy, as well as a monovalent hydrocarbon group having 1 to 6 carbon atoms as is the case with R^5 and R^6 , and r and
25 s are integers ranging from 0 to 4, and $(r+s)=(\text{valence of M})$.

[0070]

Specific examples of organometallic compounds (4) include;

(A) organic zirconium compounds such as tetra-n-
5 butoxyzirconium, ethylacetoacetate-zirconium-tri-n-
butylate, bis(ethylacetoacetate)-zirconium-di-n-butylate,
tris(ethylacetoacetate)-zirconium-n-butylate, tetrakis(n-
propylacetoacetate)-zirconium, tetrakis(acetylaceto-
acetate)-zirconium, and tetrakis(ethylacetoacetate)-
10 zirconium;

[0071]

(B) organic titanium compounds such as tetra-i-
propoxytitanium, bis(ethylacetoacetate)-titanium-di-i-
propylate, bis(acetylacetonate)-titanium-di-i-propylate and
15 bis(acetylacetonate)-titanium-di-i-propylate;

(C) organic aluminum compounds such as tri-i-propoxy-
aluminum, ethylacetoacetate-aluminum-di-i-propylate,
acetylacetonate-aluminum-di-i-propylate, bis(ethylaceto-
acetate)-aluminum-i-propylate, bis(acetylacetonate)-
20 aluminum-i-propylate, tris(ethylacetoacetate)-aluminum,
tris(acetylacetonate)-aluminum and bis(ethylacetoacetate)-
aluminum-monoacetylacetonate.

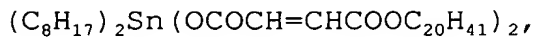
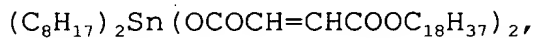
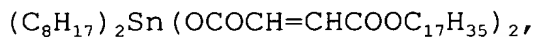
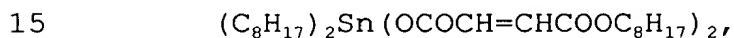
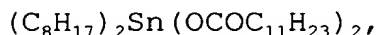
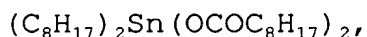
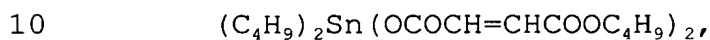
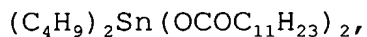
[0072]

Of these organometallic compounds (4) and partial
25 hydrolyzates thereof, preferred are ethylacetoacetate-

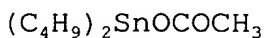
zirconium-tri-n-butylate, bis(acetylacetonate)-titanium-di-i-propylate, ethylacetoacetate-aluminum-di-i-propylate, tris(ethylacetoacetate)-aluminum and (partial) hydolyzates of these compounds.

5 [0073]

Specific examples of the organic tin compounds include; carboxylic acid type organic tin compounds such as



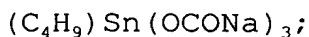
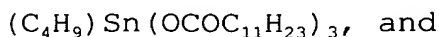
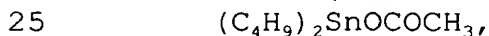
20 [0074]



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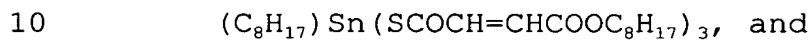
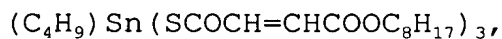
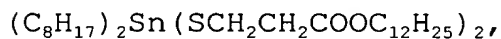
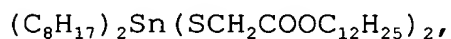
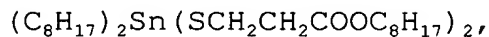
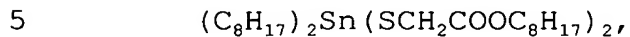
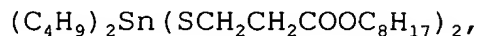
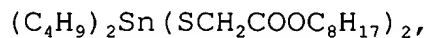
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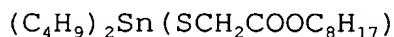


[0075]

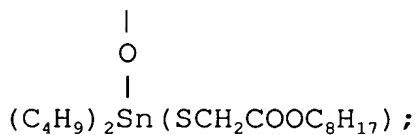
mercaptide type organic tin compounds such as



[0076]

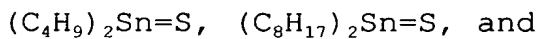


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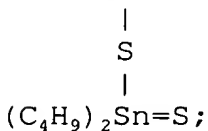
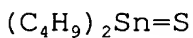


[0077]

sulfide type organic tin compounds such as



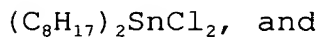
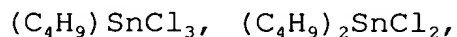
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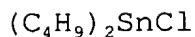


25

[0078]

chloride type organic compounds such as





5 $(\text{C}_4\text{H}_9)_2\text{SnCl}$; and

organic tin oxides such as $(\text{C}_4\text{H}_9)_2\text{SnO}$ and $(\text{C}_8\text{H}_{17})_2\text{SnO}$, and reaction products of these organic tin oxides and ester compounds such as silicate, dimethyl maleate, diethyl maleate and dioctyl phthalate.

10 [0079]

Components (g) can be used either alone or as a mixture of two or more of them, and can also be used as a mixture with zinc compounds or other reaction retardants.

[0080]

15 Component (g) may also be added in preparing the composition or at a stage where a coating layer is formed or at both the stages of the preparation of the composition and the formation of the coating layer.

In the case of the organometallic compounds, etc., the
20 amount of component (g) used is usually not more than 10 moles, preferably from 0.001 to 7 moles, and more preferably from 0.001 to 5 moles, based on mole of OR^2 contained in the above-mentioned component (a) and component (b). In this case, when the amount of component (g) used exceeds 10 moles, the composition tends
25 to deteriorate in storage stability, and cracks are liable to be developed in the resultant coating layer.

[0081]

Component (h):

Component (h) is at least one selected from the group consisting of a β -diketone and/or a β -keto ester represented by the following general formula (5), a carboxylic acid compound, 5 a dihydroxy compound, an amine compound and an oxaldehyde compound.



wherein, R^6 and R^7 each have the same meanings as given for R^6 and R^7 of the above-mentioned general formula in organometallic 10 compound (4).

Such component (h) is preferably used in combination, particularly when the organometallic compound, etc. is used as the above-mentioned component (g).

[0082]

15 Component (h) serves as a stability enhancing agent for the composition. That is to say, it is presumed that component (h) coordinates to a metallic atom in the organometallic compound, etc. to appropriately control the action for promoting the co-condensation reaction of the above-mentioned 20 components (a) to (c) according to the organometallic compound, etc., thereby acting so as to further improve the storage stability of the resultant composition.

[0083]

Specific examples of component (h) include acetylacetone, 25 methyl acetoacetate, ethyl acetoacetate, n-propyl aceto-

acetate, i-propyl acetoacetate, n-butyl acetoacetate, sec-butyl acetoacetate, t-butyl acetoacetate, hexane-2,4-dione, heptane-2,4-dione, heptane-3,5-dione, octane-2,4-dione, nonane-2,4-dione, 5-methylhexane-2,4-dione, malonic acid, oxalic acid, phthalic acid, glycolic acid, salicylic acid, aminoacetic acid, iminoacetic acid, ethylenediamine-tetraacetic acid, glycol, catechol, ethylenediamine, 2,2-bipyridine, 1,10-phenanthroline, diethylenetriamine, 2-ethanolamine, dimethylglyoxime, dithizone, methionine and salicylaldehyde. Of these, preferred are acetylacetone and ethyl acetoacetate.

Components (h) can be used either alone or as a mixture of two or more of them.

[0084]

The amount of component (h) used is usually 2 mole or more, and preferably from 3 to 20 moles, based on mole of the organometallic compound in the above-mentioned organometallic compound, etc. In this case, when the amount of component (h) used is less than 2 moles, the effect of improving the storage stability of the resultant composition becomes insufficient in some cases.

[0085]

Component (j):

Component (j) is a powder and/or a sol or a colloid of an inorganic compound, and mixed according to the desired

properties of the coating layer, with the proviso that colloidal silica and colloidal alumina, the above-mentioned components (f), are extruded from component (j).

When component (j) is in the sol or colloid form, the
5 average particle size thereof is usually from about 0.001 to about 100 μm .

[0086]

Specific examples of the compounds constituting component (j) include AlGaAs, $\text{Al}(\text{OH})_3$, Sb_2O_5 , Si_3N_4 , $\text{Sn-In}_2\text{O}_3$,
10 $\text{Sb-In}_2\text{O}_3$, MgF , CeF_3 , CeO_2 , $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, BeO , SiC , AlN , Fe , Co , Co-FeO_x , CrO_2 , Fe_4N , BaTiO_3 , $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$, Ba ferrite, SmCO_3 , YCO_5 , CeCO_5 , PrCO_5 , $\text{Sm}_2\text{CO}_{17}$, $\text{Nd}_2\text{Fe}_{14}\text{B}$, Al_4O_3 , $\alpha\text{-Si}$, SiN_4 , CoO , Sb-SnO_2 , Sb_2O_5 , MnO_2 , MnB , Co_3O_4 , Co_3B , LiTaO_3 , MgO , MgAl_2O_4 , BeAl_2O_4 , ZrSiO_4 , ZnSb , PbTe , GeSi , FeSi_2 , CrSi_2 , CoSi_2 , $\text{MnSi}_{1.73}$, Mg_2Si ,
15 $\beta\text{-B}$, BaC , BP , TiB_2 , ZrB_2 , HfB_2 , Ru_2Si_3 , TiO_2 (rutile), TiO_3 , PbTiO_3 , Al_2TiO_5 , Zn_2SiO_4 , Zr_2SiO_4 , $2\text{MgO}_2\text{-Al}_2\text{O}_3\text{-5SiO}_2$, Nb_2O_5 , $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-4SiO}_2$, Mg ferrite, Ni ferrite, Ni-Zn ferrite, Li ferrite and Sr ferrite.

These components (j) can be used either alone or as a
20 mixture of two or more of them.

[0087]

As the existing forms of component (j), there are a powder, an aqueous sol or colloid in which component (j) is dispersed in water, and a solvent sol or colloid in which component (j)
25 is dispersed in a polar solvent such as isopropyl alcohol or

a nonpolar solvent such as toluene. The solvent sol or colloid may be further diluted with water or a solvent for use depending on the dispersion stability of the semiconductor, or component (j) may be surface treated for improving the dispersion
5 stability.

[0088]

When component (j) is in the aqueous sol or colloid form, or in the solvent sol or colloid form, the solid concentration is preferably 40% by weight or less.

10 [0089]

Component (j) may also be added after the preparation of the composition or added at a stage of the preparation of the composition in order to be hydrolyzed and condensed together with component (a), component (b) and the above-mentioned
15 condensates.

[0090]

The amount of component (j) used is generally from 0 to 500 parts by weight, and preferably from 0.1 to 400 parts by weight, in terms of the solid content, based on 100 parts by
20 weight of the complete hydrolyzates/condensates of the above-mentioned component (a).

[0091]

Other Additives:

Appropriate fillers may be separately added to and
25 dispersed in the coating compositions of the present invention

for coloring and increasing the thickness of the resultant coating layers.

Such fillers include, for example, water-insoluble organic and inorganic pigments, and excluding pigments, granular, fibrous or scaly ceramics, metals and alloys, oxides, hydroxides, carbides, nitrides and sulfides of these metals.

[0092]

Specific examples of the above-mentioned fillers include iron, copper, aluminum, nickel, silver, zinc, ferrite, carbon black, stainless steel, silicon dioxide, titanium dioxide for pigment, aluminum oxide, chromium oxide, manganese oxide, iron oxide, zirconium oxide, cobalt oxide, synthetic mullite, aluminum hydroxide, iron hydroxide, silicon carbide, silicon nitride, boron nitride, clay, loam, slaked lime, gypsum, talc, barium carbonate, calcium carbonate, magnesium carbonate, barium sulfate, bentonite, mica, zinc green, chrome green, cobalt green, viridian, Guignet's green, cobalt chrome green, shale green, green soil, manganese green, pigment green, ultramarine, Prussian blue, pigment green, rocky blue, cobalt blue, cerulean blue, copper borate, molybdenum blue, copper sulfide, cobalt purple, mars violet, manganese purple, pigment violet, lead suboxide, calcium plumbate, zinc yellow, lead sulfide, chrome yellow, yellow soil, cadmium yellow, strontium yellow, titanium yellow, litharge, pigment yellow, copper suboxide, cadmium red, selenium red, chrome vermilion, Indian

red, zinc white, antimony white, basic lead sulfate, titanium white, lithopone, lead silicate, zirconium oxide, tungsten white, lead, zinc flower, Bantison white, lead phthalate, manganese white, lead sulfate, graphite, bone black, diamond
5 black, Thermatomic black, plant black, potassium titanate whisker and molybdenum disulfide.

These fillers can be used either alone or as a mixture of two or more of them.

The amount of the filler used is usually 300 parts by weight or less, based on 100 parts by weight of the total solid content of the composition.
10

[0093]

Further, the compositions of the invention can also contain other additives such as surfactants, silane coupling agents, titanium coupling agents and dyes, as well as known
15 dehydrating agents such as methyl orthoformate, methyl orthoacetate and tetraethoxysilane; dispersing agents such as poly(oxyethylene alkyl ethers), poly(oxyethylene alkyl phenyl ethers), poly(oxyethylene esters of fatty acids),
20 poly(carboxylic acid) polymer surfactants, polycarboxylates, polyphosphates, polyacrylates, polyamide esters and polyethylene glycol; thickening agents including cellulose derivatives such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose and
25 hydroxypropylmethyl cellulose, castor oil derivatives and

ferrosilicates; inorganic foaming agents such as ammonium carbonate, ammonium bicarbonate, ammonium nitrite, sodium boron hydride and calcium azide; and organic foaming agents including azo compounds such as azobisisobutyronitrile, 5 hydrazine compounds such as diphenylsulfone-3,3'-disulfohydrazine, semicarbazide compounds, triazole compounds and N-nitroso compounds, as desired.

[0094]

Further, leveling agents can be added for more improving 10 the coating performance of the coating compositions. Of such leveling agents, fluorine leveling agents include, for example, BM1000 and BM1100 (tradename, and so forth) manufactured by BM-Chemie, EFCA 772 and EFCA 777 manufactured by Efca Chemicals, a FLORENE series manufactured by Kyoeisha Kagaku Co., an FC 15 series of SUMITOMO 3M LIMITED and a FLUONAL TF series of Toho Chemical Industry Co., Ltd. Further, silicone leveling agents include, for example, a BYK series manufactured by BYK Chemie, a Sshmeggo series of Sshmegmann and Efca 30, Efca 31, Efca 34, Efca 39, Efca 83, Efca 86 and Efca 88 manufactured by Efca 20 Chemicals. Ether or ester leveling agents include, for example, Carphynol of Nisshin Kagaku Kogyo Co., Ltd. and EMARGEN and HOMOGENOL manufactured by KAO CORPORATION.

[0095]

Compounding of such leveling agents improves the finished 25 appearance of coating layers and allows uniform coating also

in the formation of thin films.

The amount of the leveling agent used is preferably from 0.01 to 5% by weight, and more preferably from 0.02 to 3% by weight, based on the whole composition.

5 [0096]

As a method for adding the leveling agent, it may also be added in preparing the composition or at a stage where a coating layer is formed or at both the stages of the preparation of the composition and the formation of the coating layer.

10 [0097]

In preparing the composition of the present invention, when component (g) and component (h) are not used, there is no particular limitation on the method for mixing each component. However, when component (g) and component (h) are used, a method
15 is preferably employed in which a mixture of components excluding component (h) from components (a) to (j) is obtained, followed by addition of component (h) thereto.

[0098]

Method for Producing Composition

20 As a method for producing the composition of the present invention, it is preferable to hydrolyze and condense at least one selected from the group consisting of components (a), (b) and (c), preferably all of components (a), (b) and (c) in the presence of (d') an aqueous dispersion of a photocatalyst having
25 a pH of 3 to 9 and (e) an organic solvent in which the content

of an organic solvent having a surface tension at 20°C of more than 260 $\mu\text{N}/\text{cm}$ is 20% by weight or less based on the whole organic solvent.

5 The use of an aqueous dispersion of a photocatalyst having a pH of 3 to 9 as component (d) results in reduced corrosiveness to a machine used in the production or coating of the resultant composition.

Further, when (e) an organic solvent in which the content of an organic solvent having a surface tension at 20°C of more
10 than 260 $\mu\text{N}/\text{cm}$ is 20% by weight or less is used as organic solvent (e), the surface tension of the whole organic solvent becomes 270 $\mu\text{N}/\text{cm}$ or less. As a result, the wettability of the resultant composition to a substrate is improved, resulting in excellent film-forming properties thereof on the substrate.

15 Further, as a method for producing the composition of the present invention, it is particularly preferred that component (a) is first hydrolyzed and condensed in the presence of the above-mentioned component (d'). This operation causes co-condensation of photocatalyst (d) with organosilane (1),
20 resulting in good compatibility with component (b), component (c) originally poor in compatibility with an aqueous dispersion of a photocatalyst, and component (e-1). Consequently, the hydrolysis/condensation of components (a) to (c) become possible in the presence of component (d) and component (e-
25 1). As a result, the dispersion stability in an organic solvent

high in surface tension such as an alcohol relatively high in hydrophobicity (for example, i-propyl alcohol or i-butyl alcohol) is improved, the storage stability of the resultant composition becomes better, the cissing phenomenon does not
5 occur on an undercoating layer and a substrate, and the film-forming properties are improved.

[0099]

Specific examples of the methods for producing the composition of the present invention include a method of adding
10 all or a part of component (a) to component (d), hydrolyzing and condensing component (a) utilizing water in component (d), then, adding components (b), (c) and (e), and the remainder of component (a) as so desired, followed by mixing, and further conducting the condensation reaction; and
15 a method of subjecting all or a part of component (a) to the hydrolysis/condensation reaction in the presence of component (d), then, sequentially adding the remainder of component (a) as so desired, and components (b), (c) and (e), followed by mixing, and conducting the condensation reaction.

20 [0100]

The total solid concentration of the composition of the present invention is generally from 3 to 50% by weight, and preferably from 5 to 40% by weight. When the total solid concentration of the composition exceeds 45% by weight, the
25 storage stability is lowered in some cases. The composition

of the present invention is usually appropriately adjusted according to its application purpose at the time of coating.

[0101]

Undercoating Composition

5 As described above, the compositions of the present invention provide the coating layers excellent in resistance to stains, coating layer durability and transparency and having photocatalytic activity. However, for preventing deterioration of substrates caused by photocatalysts and
10 further obtaining coating substrates also excellent in long-term durable adhesion, it is desirable to undercoat the following composition (i) on the substrates.

[0102]

Composition (i):

15 Composition (i) is an undercoating composition containing the above-mentioned component (a) and/or component (b) and component (c) (hereinafter also referred to as "undercoating composition (i)" or "composition (i)"). Composition (i) may contain the above-mentioned component (f).

20 [0103]

 In composition (i), the above-mentioned components (a) to (c) are preferably co-condensed in the presence of water and/or an organic solvent. In this case, the amount of water used is usually 0.3 mole or more, and preferably from about 0.4
25 to about 2 moles, based on total mole of organosilane (1) and

component (b).

Component (i) is usually supplied in the form of a solution or dispersion in water and/or an organic solvent. There is no particular limitation on the organic solvent, as
5 long as it can mix each component homogeneously. Examples of the solvents include alcohols, aromatic hydrocarbons, ethers, ketones and esters.

Of these organic solvents, specific examples of the alcohols include methanol, ethanol, n-propyl alcohol, i-propyl
10 alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, n-hexyl alcohol, n-octyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether acetate, diethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene
15 monomethyl ether acetate and diacetone alcohol.

[0104]

Further, specific examples of the aromatic hydrocarbons include benzene, toluene and xylene; specific examples of the ethers include tetrahydrofuran and dioxane; specific examples
20 of the ketones include acetone, methyl ethyl ketone, methyl isobutyl ketone and diisobutyl ketone; and specific examples of the esters include ethyl acetate, propyl acetate, butyl acetate and propylene carbonate.

These organic solvents can be used either alone or as a
25 mixture of two or more of them.

Component (i) can further contain the above-mentioned components (g) to (j) as required. Furthermore, for improving weather resistance and long-term durable adhesion, component (i) may contain ultraviolet absorbers and/or ultraviolet stabilizers. Specific examples of the ultraviolet absorbers include inorganic semiconductors such as ZnO_2 , TiO_2 and CeO_2 ; organic ultraviolet absorbers such as salicylic acids type, benzophenone type, benzotriazole type, cyanoacrylate type and triazine type. Specific examples of the ultraviolet stabilizers include piperidine type ultraviolet stabilizers.

Other resins may be blended with composition (i). The other resins include acrylic-urethane resins, epoxy resins, polyester resins, acrylic resins, fluororesins, acrylic resin emulsions, epoxy resin emulsions, polyurethane emulsions and polyester emulsions.

The total solid concentration of the above-mentioned undercoating composition (i) is usually 50% by weight or less, and preferably 40% by weight or less. It is appropriately adjusted according to the kind of substrate, the coating method and the coating layer thickness.

[0105]

Cured Product

The cured product obtained by use of the composition of the present invention has, for example, the following structure:

- (1) Substrate/coating composition of the invention;
(2) Substrate/undercoating composition (i)/coating composition of the invention;
(3) Substrate/primer/coating composition of the invention; or
(4) Substrate/primer/undercoating composition (i)/coating composition of the invention.

[0106]

Means used for coating the substrate with any one of the compositions of the present invention include means using a brush, a roll coater, a flow coater, a centrifugal coater, an ultrasonic coater and a (micro) gravure coater; dip coating, flow coating, spray coating, a screen process, electro-deposition and vapor deposition.

[0107]

In the case of the compositions of the present invention, coating layers having a thickness of about 0.05 to about 20 μm in one application or a thickness of about 0.1 to about 40 μm in two applications, in dry thickness, can be formed. Then, the compositions applied onto the substrates are dried at room temperature, or heated at a temperature of about 30°C to about 200°C for about 1 to 60 minutes to dry them. Thus, the coating layers can be formed.

[0108]

When the undercoating is preliminarily applied, the

above-mentioned compositions (i) to (iv) are preferably used. As coating methods of compositions (i) to (iv), there can be used the above-mentioned methods for coating the substrates with the compositions of the present invention. Coating layers
5 having a thickness of from about 0.05 to about 40 μm in one application or a thickness of from about 0.1 to about 80 μm in two or three applications, in dry thickness, can be formed. Then, the coating layers are dried at ordinary temperature, or dried by heating at about 30 to about 200°C usually for about
10 0.5 to about 60 minutes, thereby being able to form coating layers on various substrates.

The total thickness of the undercoat layer and the overcoat layer is usually from about 0.1 to about 80 μm , and preferably from about 0.2 to about 60 μm , in dried thickness.

15 [0109]
Substrate

Materials for the substrates to which the compositions of the present invention are applicable include, for example, metals such as iron, aluminum and stainless steel; inorganic
20 ceramic materials such as cement, concrete, ALC, flexible boards, mortar, slate, gypsum, ceramics and brick; shaped articles of plastics such as phenol resins, epoxy resins, polyesters, polycarbonates (PC), polyethylene, polypropylene and ABS resins (acrylonitrile-butadiene-styrene resins);
25 films of plastics such as polyethylene, polypropylene,

polyvinyl alcohol, polycarbonates, polyethylene terephthalate (PET), polyurethanes and polyimides; wood; paper; and glass. The compositions of the present invention are also useful for repainting of deteriorated coating layers.

5 [0110]

The substrates can also be preliminarily surface treated for base preparation, improvement in adhesion, sealing of porous substrates, smoothing and patterning.

The surface treatments to the metallic substrates include, 10 for example, polishing, degreasing, plating treatment, chromate treatment, flame treatment and coupling treatment. The surface treatments to the plastic substrates include, for example, blast treatment, treatment with chemicals, degreasing, flame treatment, oxidation treatment, vapor treatment, corona 15 discharge treatment, ultraviolet irradiation treatment, plasma treatment and ion treatment. Further, the surface treatments to the inorganic ceramic substrates include, for example, polishing, sealing and patterning. Still further, the surface treatments to the wood substrates include, for 20 example, polishing, sealing and insect proofing treatment. Furthermore, the surface treatments to the paper substrates include, for example, sealing and insect proofing treatment. The surface treatments to the deteriorated coating layers include, for example, polishing.

25 [0111]

The coating operation of the composition of the present invention varies depending on the kind and state of substrate and the coating method. For example, in the case of the metallic substrates, primers are used in addition to undercoating composition, if rust prevention is required. In the case of the inorganic ceramic substrates, the covering properties of the coating layers vary depending on the characteristics (such as surface roughness, impregnation properties and alkalinity) of the substrates, so that primers are employed in some cases. Further, in repainting deteriorated coating layers, when the deterioration of the old coating layers is significant, primers are used.

In the case of other substrates such as plastics, wood, paper and glass, primers may be used or not, depending on their application.

[0112]

There is no particular limitation on the kind of primer, as long as it has the function of enhancing the adhesion between the substrate and the composition, and it is selected depending on the kind and application purpose of substrate. The primers can be used either alone or as a mixture of two or more of them. They may be either enamel containing coloring components, or clear one containing no coloring components.

[0113]

Examples of the primers include alkyd resins, aminoalkyd

resins, epoxy resins, polyesters, acrylic resins, urethane resins, fluororesins, acrylic silicone resins, acrylic resin emulsions, epoxy resin emulsions, polyurethane emulsions and polyester emulsions. When the adhesion is required between the
5 substrates and the coating layers under severe conditions, various functional groups can also be imparted to these primers. Such functional groups include, for example, a hydroxyl group, a carboxyl group, a carbonyl group, an amido group, an amine group, a glycidyl group, an alkoxysilyl group, an ether bond
10 and an ester bond. The primers may also contain ultraviolet ray absorbers and ultraviolet ray stabilizers.

[0114]

For the purpose of increasing the abrasion resistance and the glossiness of the coating layers, clear layers composed of,
15 for example, siloxane resin paints such as stable dispersions of colloidal silica and siloxane resins disclosed in US Patent Nos. 3,986,997 and 4,027,073 can also be formed on surfaces of the coating layers formed of the compositions of the present invention.

20 [0115]

According to the coating compositions of the present invention, coating of exterior materials, road materials, interior materials, fibers and so on, as well as above
substrates, can form coating layers high in hardness and
25 excellent in weather resistance, coating layer durability,

resistance to alkalis, resistance to organic chemicals and resistance to stains.

[0116]

[EXAMPLES]

5 The invention will be illustrated with reference to examples in more detail below, but the following examples are not intended to limit the scope of the invention. Parts and percentages in the examples and comparative examples are on a weight basis, unless otherwise specified. Various
10 measurements and evaluations in the examples and comparative examples were made as follows.

[0117]

(1) Mw

The Mw was measured by gel permeation chromatography
15 (GPC) according to the following conditions:

Sample: Using tetrahydrofuran as a solvent, a sample was prepared by dissolving 1 g of an organosilane hydrolyzate/condensate or 0.1 g of a silyl group-containing polymer to be measured in 100 cc of tetrahydrofuran.

20 Standard polystyrene: Standard polystyrene manufactured by Pressure Chemical Co., Ltd., USA was used.

Apparatus: High temperature and high speed gel permeation chromatogram (model 150-C ALC/GPC, manufactured by Waters Co., Ltd., USA);

25 Column: SHODEX A-80M (50 cm in length) manufactured by

Showa Denko K.K.;

Measuring temperature: 40°C;

Flow rate: 1 cc/minute.

[0118]

5 (2) Storage Stability

A composition having no curing accelerator was stored in a polyethylene bottle in the sealed state at ordinary temperature for 3 months, and the presence or absence of gelation was visually judged. For the composition in which no
10 gelation occurred, the viscosity was measured with a BM type viscometer manufactured by Tokimec Co., Ltd. When the rate of change thereof was within 20%, it was indicated as ○ (no change).

(3) Hardness

15 The hardness was measured based on the pencil hardness according to JIS K5400.

(4) Resistance to Alkalis

After a test piece was immersed in a saturated aqueous solution of calcium hydroxide for 60 days, the state of a coating
20 layer was visually observed.

[0119]

(5) Resistance to Organic Chemicals

Isopropyl alcohol was dropped in an amount of 2 cc onto a coating layer, and wiped off with cloth after 5 minutes. Then,
25 the state of the coating layer was visually observed.

(6) Resistance to Moisture

A test piece was continuously kept under the circumstances of 50°C (temperature) and 95% (moisture) for 1,000 hours. Then, the test piece was taken out, and the state of a coating layer was visually observed.

(7) Resistance to Weather

A 2,000-hour irradiation test was carried out with a Sunshine weather meter according to JIS K5400, and the state of appearance (cracking, peeling and so forth) of a coating layer was visually observed.

[0120]

(8) Resistance to Water

After a test piece was immersed in tap water at room temperature for 60 days, the state of a coating layer was visually observed.

(9) Resistance to Stains

A paste composed of a mixture of carbon black/kerosine oil=1/2 (in weight ratio) was applied onto a coating layer, and allowed to stand at room temperature for 24 hours, followed by washing with water using a sponge. The stained state of a coating layer was visually observed, and evaluated on the basis of the following criteria:

○: Not stained

△: Slightly stained

×: Terribly stained.

[0121]

(10) Transparency

Each composition was applied onto quartz glass so as to give a dry thickness of 1 μm . Then, the transparency of visible
5 light was measured, and evaluated on the basis of the following criteria:

◎: The permeability exceeded 80%.

○: The permeability was from 60% to 80%.

△: The permeability was less than 60%.

10 (11) Hydrophilicity

After a coating layer was irradiated at a rate of 1.0 mW/cm² with a black-light fluorescent lamp for 72 hours, the contact angle (unit: degree) of water was measured.

(12) Adhesion

15 A tape peeling test was conducted three times by the cross-cut adhesion test (100 cross cuts) according to JIS K5400, and adhesion was based on an average thereof.

[0122]

Reference Example 1 (Synthesis of Component (c))

20 In a reaction vessel equipped with a stirrer and a reflux condenser, 55 parts of methyl methacrylate, 5 parts of 2-ethylhexyl acrylate, 5 parts of cyclohexyl methacrylate, 10 parts of γ -methacryloxypropyltrimethoxysilane, 20 parts of glycidyl methacrylate, 5 parts of 4-(meth)acryloyloxy-
25 2,2,6,6-tetramethylpiperidine, 75 parts of i-butyl alcohol,

50 parts of methyl ethyl ketone and 25 parts of methanol were placed and mixed. Then, the mixture was heated to 80°C with stirring, and a solution of 3 parts of azobisisovaleronitrile in 8 parts of xylene was added dropwise to the mixture for 30 minutes, followed by reaction at 80°C for 5 hours. Thus, a polymer solution having a solid concentration of 40% (hereinafter referred to as "(c-A)") was obtained, the polymer having an Mw of 12,000.

[0123]

10 Reference Example 2 (Synthesis of Component (c))

In a reaction vessel equipped with a stirrer and a reflux condenser, 55 parts of methyl methacrylate, 5 parts of 2-ethylhexyl acrylate, 5 parts of cyclohexyl methacrylate, 10 parts of γ -methacryloxypropyltrimethoxysilane, 20 parts of 15 2-hydroxyethyl methacrylate, 5 parts of 4-(meth)-acryloyloxy-2,2,6,6-tetramethylpiperidine, 75 parts of i-butyl alcohol, 50 parts of methyl ethyl ketone and 25 parts of methanol were placed and mixed. Then, the mixture was heated to 80°C with stirring, and a solution of 3 parts of 20 azobisisovaleronitrile in 8 parts of xylene was added dropwise to the mixture for 30 minutes, followed by reaction at 80°C for 5 hours. Thus, a polymer solution having a solid concentration of 40% (hereinafter referred to as "(c-B)") was obtained, the polymer having an Mw of 13,000.

25 [0124]

Reference Example 3 (Synthesis of Component (c))

In a reaction vessel equipped with a stirrer and a reflux condenser, 30 parts of methyl methacrylate, 10 parts of n-butyl acrylate, 10 parts of γ -methacryloxypropyltrimethoxysilane, 20 parts of glycidyl methacrylate, 10 parts of 4-(meth)acryloyloxy-2,2,6,6-tetramethylpiperidine, 20 parts of 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole, 75 parts of i-butyl alcohol, 50 parts of methyl ethyl ketone and 25 parts of methanol were placed and mixed. Then, the mixture was heated to 80°C with stirring, and a solution of 4 parts of azobisisovaleronitrile in 10 parts of xylene was added dropwise to the mixture for 30 minutes, followed by reaction at 80°C for 5 hours. Then, 83 parts of methyl ethyl ketone was added to obtain a polymer solution having a solid concentration of 30% (hereinafter referred to as "(c-C)"), the polymer having an Mw of 10,000.

[0125]

Example 1

In a reaction vessel equipped with a stirrer and a reflux condenser, 151 parts of anatase type titanium oxide dispersed in water having a solid concentration of 24.5%, a pH of 3 and an average particle size of 50 nm as component (d) and 19 parts of methyltrimethoxysilane as component (a) were placed, followed by stirring at 30°C for 1 hour. Then, 2 parts of methyltrimethoxysilane as component (a), 16 parts of an end

alkoxysilyl group/poly(oxyethylene/oxypropylene) group-
containing oligomer (Mw: 10,000) as component (b) and 4 parts
of i-propyl alcohol (surface tension at 20°C: 217 μ N/cm) as
component (e-1) were added and mixed, followed by stirring at
5 30°C for 1 hour. Further, 22 parts of methyltrimethoxysilane
as component (a), 40 parts of (c-A) as component (c) and 36 parts
of i-propyl alcohol as component (e-1) were added and mixed,
followed by stirring at 30°C for 1 hour. Then, 2 parts of
ethylacetoacetate-aluminum-di-i-propylate as component (g)
10 dissolved in 10 parts of i-propyl alcohol was added and mixed,
followed by co-condensation reaction at 60°C for 4 hours with
stirring.

Thereafter, 2 parts of acetylacetone was added as
component (h), and stirred for 1 hour, followed by cooling to
15 room temperature. Then, 600 parts of i-propyl alcohol (e-1)
was added to obtain composition I-1 having a solid concentration
of about 10%. Components of the composition prepared are shown
in Table 1.

[0126]

20 Examples 2 to 6

Compositions were prepared in the same manner as with
Example 1 with the exception that respective components shown
in Table 1 were used. When colloidal silica dispersed in
methanol (solid concentration: 10%), component (f), was added
25 as an additional component, it was added after cooling to room

temperature and addition of the diluent.

Prepared compositions were shown in Table 1.

Of the used organic solvents shown in Table 1, ethylene glycol monobutyl ether has a surface tension (20°C) of 274 $\mu\text{N}/\text{cm}$,
5 and diethylene glycol monoethyl ether has a surface tension (20°C) of 318 $\mu\text{N}/\text{cm}$.

[0127]

[TABLE 1] (to be continued)

Example	1	2	3	4	5	6
Name of Composition	I-1	I-2	I-3	I-4	I-5	I-6
<u>Mixing Component (parts)</u>						
In Mixing at Room Temp. (1)						
Component (a): Methyltrimethoxy- silane	19	19	19	13	13	183
Component (d): Aqueous Dispersion of Titanium Oxide (solid conc.: 24.5%)	151	151	151	105	105	147
In Mixing at Room Temp. (2)						
Component (a): Methyltrimethoxysilane	2	2	2	15	15	22
Component (b): End alkoxysilyl group-containing trifunctional oligomer (Mw = 1,000)	0	16	0	0	0	0
End alkoxysilyl group/poly(oxy- ethylene/oxypropylene) group- containing bifunctional oligomer (Mw 10,000)	16	0	10	19	19	16
Component (e): i-Propyl Alcohol	4	4	4	26	26	15
In Mixing at Room Temp. (3)						
Component (a): Methyltrimethoxysilane	22	22	22	24	24	20
Dimethyldimethoxysilane	0	0	10	0	0	0
Component (c): c-A	40	0	40	48	48	20
c-B	0	40	0	0	0	0
c-C	0	0	0	0	0	0
Component (e): i-Propyl Alcohol	36	36	32	40	40	32
In Condensation Reaction						
Component (g): Ethylacetoacetate- aluminum-di-i-propylate	2	2	2	3	3	3
Component (e-1): i-Propyl Alcohol	10	10	10	13	13	15

[TABLE 1] (continued)

Example	1	2	3	4	5	6
Name of Composition	I-1	I-2	I-3	I-4	I-5	I-6
After-Addition Component						
Component (h): Acetylacetone	2	0	2	0	0	2
Component (e-1): i-Propyl Alcohol	600	550	600	550	600	600
Component (e-2):						
Ethylene Glycol Monobutyl Ether	0	0	0	50	0	0
Diethylene Glycol Monoethyl Ether	0	50	0	0	0	0
Additional Component						
Colloidal Silica (dispersion in methanol 10%)	0	0	0	0	200	0

[0128]

Preparation Example 1 (Preparation of Undercoating Composition)

5 In a reaction vessel equipped with a stirrer and a reflux condenser, 71 parts of methyltrimethoxysilane and 24 parts of dimethyldimethoxysilane as component (a), 125 parts of (c-A) having a solid concentration of 40% as component (c), 3 parts of ethylacetoacetate-aluminum-di-i-propylate as component (g),
 10 34 parts of i-propyl alcohol and 15 parts of methyl ethyl ketone were placed and mixed. The temperature of the mixture was elevated to 50°C with stirring.

Then, 17 parts of water was continuously added for 30 minutes, followed by reaction at 60°C for 4 hours.

15 Then, 4 parts of acetylacetone was added as component (h), and stirred for 1 hour, followed by cooling to room temperature. Thereafter, 190 parts of methyl ethyl ketone, 75 parts of butyl acetate, 20 parts of ethylene glycol monobutyl ether and 95

parts of isopropyl alcohol were added with stirring to obtain undercoating composition (i-1). Respective components of the composition thus prepared are shown in Table 2.

[0129]

5 Preparation Examples 2 to 6 (Preparation of Undercoating Compositions)

Undercoating compositions were obtained in the same manner as with Preparation Example 1 with the exception that respective components shown in Table 2 were used. When
10 colloidal silica dispersed in isopropyl alcohol (solid concentration: 15%) or CeO_2 dispersed in isobutyl alcohol was added as another additive, it was added after cooling to room temperature and addition of the diluting solvent. Prepared undercoating compositions were shown in Table 2.

[0130]

[TABLE 2]

Preparation Example	1	2	3	4	5	6
Name of Composition	i-1	i-2	i-3	i-4	i-5	i-6
<u>Mixing Component (parts)</u>						
Component (a):						
Methyltrimethoxysilane	71	71	71	51	41	41
Dimethyldimethoxysilane	24	24	24	0	16	16
Component (b):						
End alkoxyisilyl group-containing oligomer (Mw = 3,000)	0	0	0	25	0	0
Component (c):						
(c-A) solid conc.: 40%	125	0	0	125	175	175
(c-B) solid conc.: 40%	0	125	0	0	0	0
(c-C) solid conc.: 30%	0	0	167	0	0	0
Added in Reaction						
Water	17	17	17	10	10	10
Methyl Isobutyl Ketone	0	0	54	0	0	0
Methyl Ethyl Ketone	15	15	0	37	13	13
i-Propyl Alcohol	34	34	0	37	31	31
Added after Completion of Reaction and Cooling						
Methyl Isobutyl Ketone	0	0	100	80	0	0
Methyl Ethyl Ketone	190	190	200	200	190	190
Butyl Acetate	75	75	0	0	75	95
Ethylene Glycol Monobutyl Ether	20	20	34	20	20	0
i-Propyl Alcohol	95	95	0	82	95	95
Component (g): Ethylacetoacetate-aluminum-di-i-propylate	3	3	5	3	3	3
<u>After-Addition Component</u>						
Component (h): Acetylacetone	4	4	6	4	4	4
Additional Component						
Component (f): Colloidal Silica Dispersed in i-Propyl Alcohol (solid conc.: 15%)	0	200	0	0	200	0
Component (j): CeO ₂ Dispersed in i-Butyl Alcohol (solid conc.: 15%)	0	0	0	0	0	200

[0131]

Examples 7 to 12

To 100 parts of each coating composition of the present invention, 3 parts of a solution of a reaction product of dibutyl tin diacetate and silicate oligomer in i-propyl alcohol (solid content: 15%) was added and sufficiently stirred. The resultant composition was applied onto quartz glass and dried so as to give a dry thickness of 0.2 μm to obtain a cured product. For each cured product thus obtained, various evaluations were carried out. Results thereof are shown in Table 3.

[0132]

10 [TABLE 3]

Example	7	8	9	10	11	12
Composition of the Invention	I-1	I-2	I-3	I-4	I-5	I-6
Storage Stability	○	○	○	○	○	○
Pencil Hardness	4H	4H	4H	4H	4H	4H
Resistance to Alkalis	Good	Good	Good	Good	Good	Good
Resistance to organic chemicals	Good	Good	Good	Good	Good	Good
Resistance to Moisture	Good	Good	Good	Good	Good	Good
Resistance to Weather	Good	Good	Good	Good	Good	Good
Resistance to Water	Good	Good	Good	Good	Good	Good
Resistance to Stains	◎	◎	◎	◎	◎	◎
Transparency	○	○	○	○	○	○
Hydrophilicity (degree)	4	3	2	3	2	3

[0133]

Examples 13 to 46

To 100 parts of each of undercoating compositions (i-1) to (i-6), 10 parts of a solution of dioctyl tin dimaleate ester in i-propyl alcohol (solid content: 10%) was added if necessary, followed by sufficient stirring. The resultant

composition was applied onto each substrate shown in Tables 4 to 6, and dried so as to give a dry thickness of 2 μm . Then, a composition obtained by adding 3 parts of a solution of a reaction product of dibutyl tin diacetate and silicate oligomer in i-propyl alcohol (solid content: 15%) to 100 parts of each of the overcoating compositions of the present invention and sufficiently stirring the resultant mixture was applied thereon and dried so as to give a coating layer having a dry thickness of 0.2 μm to prepare a cured product. Adhesion and resistance to weather were evaluated for the resultant cured products. Results thereof are shown together in Tables 4 to 6. In examples in which two kinds of undercoating compositions were used, the compositions were provided on the substrate as a plurality of undercoat layers without mixing them, thereby specifying the total thickness.

[0134]

[TABLE 4]

Example	Substrate	Under-coating Composition	Photocatalyst-Containing Composition of the Invention	Adhesion	Resistance to Weather
13	PET Film (thickness: 50 μ m, surface-treated with modified acrylic resin)	i-3	I-1	100	Good
14		i-3	I-2	100	Good
15		i-3	I-3	100	Good
16		i-3	I-4	100	Good
17		i-3	I-5	100	Good
18		i-3	I-6	100	Good
19		i-6	I-1	100	Good
20		i-6	I-2	100	Good
21		i-6	I-3	100	Good
22		i-6	I-4	100	Good
23		i-6	I-5	100	Good
24		i-6	I-6	100	Good
25		i-6	I-7	100	Good
26	PMMA Plate (thickness: 2 mm)	i-1	I-1	100	Good
27		i-2	I-1	100	Good
28		i-3	I-1	100	Good
29		i-4	I-1	100	Good
30		i-5	I-1	100	Good
31		i-6	I-1	100	Good

[0135]

[TABLE 5]

Example	Substrate	Undercoating Composition	Photocatalyst-Containing Composition of the Invention	Adhesion	Resistance to Weather
32	Acrylic Resin Film (thickness: 50 μ m)	i-5	I-1	100	Good
33		i-5	I-6	100	Good
34		i-6	I-1	100	Good
35		i-6	I-6	100	Good
36	PC Plate (thickness: 2 mm)	i-3	I-1	100	Good
37		i-3	I-2	100	Good
38		i-6	I-3	100	Good
39		i-6	I-4	100	Good
40		i-6	I-5	100	Good
41	ABS Plate	i-1	I-1	100	Good
42	Inorganic Ceramic Substrate (12 mm)	Epoxy resin (0.5 μ m) /i-1	I-1	100	Good
43	Foamed Concrete (ALC)	Epoxy resin (0.5 μ m) /I-1	I-6	100	Good

[0136]

[TABLE 6]

Example	Substrate	Undercoating Composition	Photocatalyst-Containing Composition of the Invention	Adhesion	Resistance to Weather
44	Tile	i-1	I-6	100	Good
45	Glass	i-5	I-1	100	Good
46	wood	Polyester emulsion (0.5 μ m) /i-5	I-1	100	Good

5

[0137]

[EFFECTS OF THE INVENTION]

The coating composition of the present invention is

excellent in dispersion stability of a photocatalyst, excellent in storage stability, giving a coating layer excellent in durability and adhesion, and having a photocatalytic function.

[NAME OF DOCUMENT] Abstract

[SUMMARY]

[PROBLEM] To obtain a coating composition excellent in dispersion stability of a photocatalyst, excellent in storage stability, giving a coating layer excellent in durability and adhesion, and having a photocatalytic function.

[MEANS FOR SOLVING PROBLEM] A coating composition comprises (a) at least one component selected from the group consisting of an organosilane represented by $(R^1)_nSi(OR^2)_{4-n}$ (wherein, R^1 represents a monovalent organic group; R^2 represents an alkyl group or an acyl group; and n is an integer ranging from 0 to 2), and a hydrolyzate thereof; (b) an organosiloxane oligomer having an SiO bond and a weight average molecular weight of 300 to 100,000, (c) a polymer containing a silyl group having a silicon atom bound to a hydrolytic group and/or a hydroxyl group, (d) a photocatalyst, and (e-1) an organic solvent having a surface tension at 20°C of 260 $\mu N/cm$ or less.

[CHOSEN DRAWING] None